

Scintillation properties of pure and Ce³⁺-doped SrF₂ crystals

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Abstract

In this paper results of scintillation properties measurements of pure and Ce³⁺-doped strontium fluoride crystals are presented. We measure light output, scintillation decay time profile and temperature stability of light output. X-ray excited luminescence outputs corrected for spectral response of monochromator and photomultiplier for pure SrF₂ and SrF₂-0.3 mol.% Ce³⁺ are approximately 95% and 115% of NaI-Tl emission output, respectively. A photopeak with a 10% full width at half maximum is observed at approximately 84% the light output of a NaI-Tl crystal after correction for spectral response of photomultiplier, when sample 10x10 mm of pure SrF₂ crystal is excited with 662 KeV photons. Corrected light output of SrF₂-0.3 mol.% Ce³⁺ under 662 KeV photon excitation is found at approximately 64% the light output of the NaI-Tl crystal.

Keywords: scintillator, well-logging, alkali-earth fluorides, cerium doped crystals

1. Introduction

The interest in new scintillation materials is promoted by increasing number of new applications in medicine, science, and homeland security, which require ramp-up of material production. The most perspective scintillators are bromides and iodides doped with Ce³⁺ and Eu²⁺ ions, such as SrI₂-Eu and LaBr₃-Ce. These crystals have high light outputs (up to 100000 photons/MeV for SrI₂-Eu), good energy resolution, and high proportionality (Dorenbos, 2010). Disadvantages of these scintillators are high hygroscopic and price. In addition, SrI₂-Eu has temperature instability of light output observed by Alekhin et al., 2011.

For the most applications a cheaper NaI-Tl scintillator has quite properties (light output about 45000 photons/MeV cited in Derenzo, 2012). Therefore, one of the way in development of new scintillators is to find new materials with similar to NaI-Tl properties but no hygroscopic. In this way advanced materials for new scintillators are alkali-earth fluorides doped with rare earth ions. Theoretical limit of light output for them is up to 50000 photons/MeV (Dorenbos, 2010). If an efficient energy transfer is provided then alkali-earth fluorides will be promising scintillators. A real light output of CaF₂-Eu is 18000-22000 photons/MeV, but BaF₂ and BaF₂-Ce crystals demonstrate lower light output at about 10000 photons/MeV (Visser et al., 1991). Scintillation properties of SrF₂ crystals are almost not investigated. Light output of SrF₂ was estimated about 10000-12000 photons/MeV by Schotanus et al., 1987. However, potential light output of SrF₂ will be higher. Also SrF₂ crystals doped with Ce³⁺ and Pr³⁺ have a temperature stability

of light output in wide range (20 °C to 200 °C) (Shendrik and Radzhabov, 2010). Therefore, SrF₂ can be high-potential scintillator for well-logging. So, scintillator properties of strontium fluoride crystals are among the least studied of fluorides crystals, but these crystals have potential applications. Thus, the investigations of scintillation properties of strontium fluorides are topical today. This paper describes the scintillation properties of pure and cerium doped strontium fluorides crystals, a newly discovered inorganic scintillator.

2. Experimental methodology

Growing with addition of CdF₂ as an oxygen scavenger, oxygen-free crystals of pure SrF₂ and doped with different concentrations of Ce³⁺ ions were grown in a graphite crucible by the Stockbarger method. We applied several experimental techniques in measurement of scintillation properties of the crystals. To determine light output, pulsed-height spectra under ¹³⁷Cs 662 KeV gamma source excitation were measured with PMT FEU-39A, a homemade preamplifier and an Ortec 570A spectrometric amplifier. The crystals of 10x10 mm dimensions were polished and then covered with several layers of ultraviolet reflecting Teflon tape (PTFE tape). The shaping time of Ortec 570 spectrometric amplifier was set at 10 μs to collect much light from scintillator.

X-ray excited luminescence was performed using x-ray tube with Pd anode operating at 35 kV and 0.8 mA. The spectra were recorded at photon-counting regime using PMT FEU-39A and vacuum grating monochromator VM-4.

Scintillation decay time profiles under ¹³⁷Cs E=662 KeV gamma source excitation were recorded by 200 MHz oscilloscope Rigol DS-1202CA. To register decay curves in wide time interval, we used oscilloscope input resistance set (50 Ω and 2.8 kΩ).

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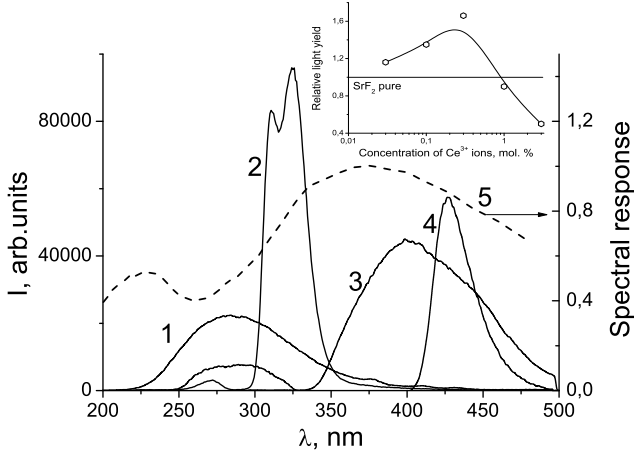


Figure 1: Luminescence spectra of SrF_2 (curve 1), SrF_2 -0.3 mol.% Ce^{3+} (curve 2), NaI-Tl (curve 3), and CaF_2 -0.1 mol.% Eu^{2+} (curve 4) under x-ray excitation. Dashed curve 5 is spectral sensitivity of the grating monochromator and PMT registration channel. In the inset dependence of integral intensity of emission bands of Ce^{3+} ions versus Ce concentration is presented.

3. Experimental results and discussion

Figure 1 shows spectra of x-ray luminescence of pure SrF_2 , NaI-Tl, SrF_2 -0.3 mol.% Ce^{3+} , and CaF_2 -0.1 mol.% Eu^{2+} . In the spectrum of SrF_2 a wide band at 280 nm is attributed to self-trapped exciton (STE) emission. In SrF_2 doped with Ce^{3+} ions STE luminescence is quenched and vanished at concentrations Ce^{3+} ions higher than 1 mol. %. The most intense bands in x-ray luminescence spectra of SrF_2 - Ce^{3+} crystal at 310 and 325 nm correspond to 5d-4f emission of Ce^{3+} ions.

Luminescence spectrum of CaF_2 - Eu^{2+} is shown in Fig. 1, curve 4. Its emission band is centered at 425 nm. This luminescence is due to $4f^65d^1-4f^7$ transitions in the Eu^{2+} ion (Kobayasi et al., 1980).

Dependence of integral intensity of Ce^{3+} ions emission bands on Ce concentration is shown in the inset to Figure 1. The highest light output is demonstrated by SrF_2 -0.3 mol.% Ce^{3+} .

X-ray excited luminescence output measured by integral intensity is compared with the one of NaI-Tl crystal (Table 1). Light output of NaI-Tl crystals is approximately 43000 photons/MeV. Therefore, light output of the measured samples can be estimated. The data are shown in Table 1. Light output of CaF_2 -0.1 mol.% Eu^{2+} is about 21500 photons/MeV that is in according with known data for CaF_2 -Eu crystals given by Derenzo, 2012. Pure SrF_2 has light output about 20640 photons/MeV, doped with 0.3 mol.% and 1 mol.% crystals have the ones about 34000 photons/MeV and 18500 photons/MeV, respectively.

All integral intensities and light outputs are presented without correction for spectral response of registration channel. The spectral response curve is shown in Figure 1, dashed line. The sensitivity of the PMT and monochromator system in SrF_2 and SrF_2 -Ce luminescence spectral range is lower than in NaI-Tl and CaF_2 -Eu emission region. After the correction, light output of pure SrF_2 luminescence is about 40000 photons/MeV, and SrF_2 doped with 0.3 mol. % and 1 mol. % crystals have light

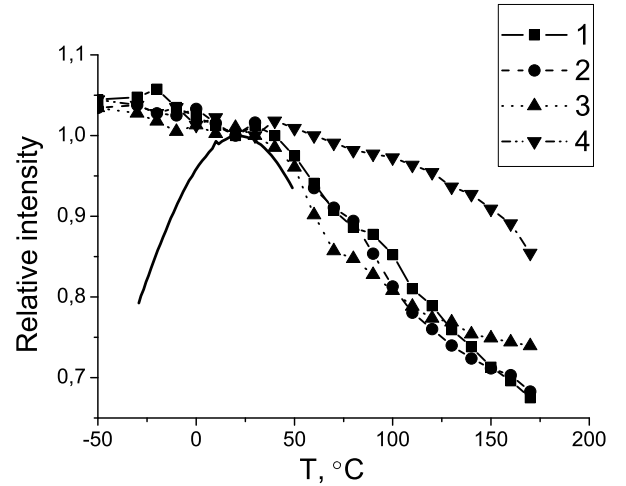


Figure 2: Temperature dependences of relative light output of SrF_2 crystals doped with 0.01 mol. % Ce^{3+} (curve 1); 0.1 mol. % Ce^{3+} (curve 2); 0.3 mol. % Ce^{3+} (curve 3) and 1 mol. % Ce^{3+} (curve 4) in comparison with NaI-Tl (solid line) measured by Moszynski et al., 2006.

outputs about 50000 photons/MeV and 28000 photons/MeV, respectively.

Temperature dependences of x-ray excited luminescence intensity of SrF_2 -Ce are given in Figure 2. Emission intensity does not depend on temperature in the range between -50 °C and +50 °C. At higher temperatures decrease of 5d-4f luminescence intensity is observed. At 170 °C temperature light output of SrF_2 doped with 0.01 mol.% and 0.1 mol.% of Ce^{3+} ions decreases to 30 %, 25 % and 15 % decreases in integral emission are found in the SrF_2 crystals doped with 0.3 mol. % Ce^{3+} and 1 mol. %, respectively. Crystals of SrF_2 -0.3 mol. % Ce^{3+} and SrF_2 -1 mol. % Ce^{3+} demonstrate high temperature stability of light output in the region between -50 °C and 170 °C in comparison with NaI-Tl (see Fig. 2, solid line). For this reason, the SrF_2 - Ce^{3+} crystals would be perspective scintillators for well-logging applications.

Figure 3 shows pulse height spectra of SrF_2 , SrF_2 -0.3 mol. % Ce^{3+} and NaI-Tl. The photopeak corresponding to the ^{137}Cs energy photon is seen in each curve in the Figure 3. Light output of SrF_2 and SrF_2 -Ce crystals was measured by comparing these response to 662 KeV energy to the response of NaI-Tl crystal with known characteristics under the same conditions. The photopeak in pure SrF_2 is centered at a pulse height that is 42% of the 662 keV photopeak pulse height in NaI-Tl. Using the NaI-Tl light output of 43000 photons/MeV, this implies that the light output of pure SrF_2 is approximately 18000 photons/MeV that is similar to x-ray emission light output (see Table 1). The full width at half maximum (FWHM) in pure SrF_2 of the 662 keV photopeak is 10 %. FWHM of NaI-Tl is 6.7 %, which is consistent with known results given by scintillators database of Derenzo, 2012.

Dependence of SrF_2 -Ce relative light output versus concentration is demonstrated in the inset to Figure 3. Best light out-

Table 1: Light output of SrF_2 , $\text{SrF}_2\text{-Ce}^{3+}$, NaI-Tl and $\text{CaF}_2\text{-0.1 mol.\% Eu}^{2+}$ crystals measured under gamma and x-ray excitation.

Crystal	Light output of x-ray excited luminescence spectra		Light output measured by pulse height spectra	
	rel.units	photons/MeV	rel.units	photons/MeV
NaI-Tl	1	43000	1	43000
$\text{CaF}_2\text{-0.1 mol.\% Eu}^{2+}$	0.5	21500	0.44	18920
SrF_2	0.48	20640	0.42	18060
$\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$	0.79	33970	0.32	13760
$\text{SrF}_2\text{-1 mol.\% Ce}^{3+}$	0.43	18490	0.2	8600

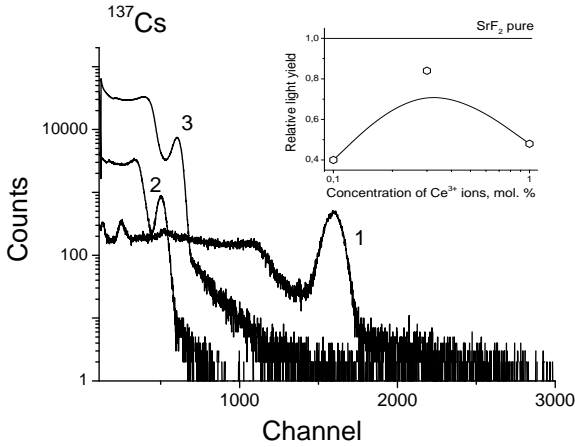


Figure 3: Pulse height spectra of NaI-Tl (curve 1), $\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$ (curve 2) and SrF_2 (curve 3) under gamma-source ^{137}Cs ($E=662 \text{ KeV}$) excitation. In the inset dependence of relative light outputs of $\text{SrF}_2\text{-Ce}$ crystals versus Ce concentration is presented.

put of the Ce -doped crystals is found for $\text{SrF}_2\text{-0.3 mol. \% Ce}^{3+}$. Its photopeak is centered at a pulse height that is 32 % of the 662 keV photopeak pulse height in NaI-Tl , this implies that the light output of $\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$ is approximately 14000 photons/MeV. FWHM of the $\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$ is approximately 9.3 %, which is lower than FWHM of pure SrF_2 . This fact means that in spite of worse light output $\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$ crystal has better energy resolution in comparison with pure strontium fluoride.

All light outputs without any corrections are given in Table 1. Bearing in mind that spectral sensitivity of S20 photocathode (PMT FEU 39A) is higher at $\text{CaF}_2\text{-Eu}$ and NaI-Tl emission bands than in SrF_2 and $\text{SrF}_2\text{-Ce}$ luminescence region (Flyckt and Marmonier, 2002). Corrected light outputs of pure SrF_2 is about 80% (36000 photons/MeV) of NaI-Tl and $\text{SrF}_2\text{-0.3 mol. \% of Ce}^{3+}$ – about 60% (26000 photons/MeV) of NaI-Tl .

Scintillation decay time profile of $\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$ is shown in Figure 4. Resistance of oscilloscope input was 2.6 K Ω for registration long time decay components in Ce^{3+} emission. The decay time is described by a sum of exponents. First component (2.8 μs) in Ce^{3+} decay is integrated short components. Lifetime of the shortest one equals 130 ns at 50 Ω input resistance in $\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$ and it becomes longer with

decrease of Ce concentration. Decay constants of this component in dependence on Ce concentration are presented in the inset of the Figure 4.

Contribution of slow components to scintillation time profile is estimated. In the figure 4 exponential components of total decay curve are shown separately. There are two long time components in $\text{SrF}_2\text{-0.3 mol.\% Ce}^{3+}$ emission. 20% of the light is emitted with a 9 μs time constant, and 25% of the light is emitted with a 280 μs time constant.

Emission decay time of cerium doped alkaline-earth fluorides under optical excitation at lowest energy absorption bands is estimated about 30 ns (Visser et al., 1993; Radzhabov and Kurobori, 2004; Wojtowicz et al., 2000). Under vacuum ultraviolet excitation at exciton and higher energies regions the decay of Ce -doped fluorides became nonexponential (Wojtowicz et al., 2000). Under x-ray excitation the decay curves is also nonexponential (Fig. 4).

Whole decay curve can be described by several processes. Fast stage could be ascribed to resonance energy transition in nearest pairs of exciton and cerium ion. In the inset of the figure 4 concentration dependence of these decay constants is presented. Note that the decay becomes shorter with increasing Ce^{3+} ions concentration due to reduction of distance between exciton and activator ion with increase of cerium ions concentration.

In $\text{SrF}_2\text{-Ce}$ crystals thermoluminescence glow peaks at 200-250 K were found (Radzhabov, 2001; Maghrabi and Townsend, 2001). Broad glow peaks at higher temperatures are shifted to lower temperature with increasing concentration of Ce^{3+} ions in the SrF_2 crystal (Maghrabi and Townsend, 2001). Long stages in scintillation time profile can be attributed to thermoactivated processes related to electron or hole delayed transfer to the activator ion. A similar energy transfer mechanism has been observed in SrF_2 doped with Pr (Shendrik and Radzhabov, 2012).

Therefore, the difference in light outputs measured from x-ray luminescence and pulse height spectra is explained by presence of intensive slow components in cerium ions luminescence (see Fig. 4). They give a large contribution to total light output. Shaping time of pulse height spectrum measurement is 10 μs , and a large part of emitted light is not registered whereas a rate of x-ray excited luminescence spectra registration is amount about 1 s^{-1} that leads to much more light registration.

Light output of $\text{SrF}_2\text{-Ce}^{3+}$ samples can be increased by de-

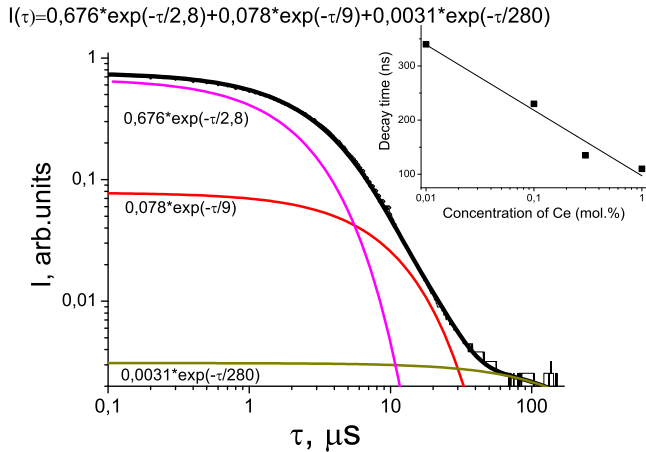


Figure 4: Scintillation decay time profile of $\text{SrF}_2\text{-}0.3 \text{ Ce}^{3+}$ crystal measured under gamma-source ^{137}Cs excitation ($E=662 \text{ KeV}$). Exponential components of total decay curve are presented separately. In the inset dependence of shortest decay time component on Ce^{3+} ions concentration is shown.

creasing of slow component contribution in Ce^{3+} luminescence. It might be possible by co-doping these crystals with Ga^{3+} , In^{3+} or Cd^{2+} ions to change band gap in $\text{SrF}_2\text{-Ce}$ crystal and, thence, reducing the role of traps in scintillation energy transfer. This idea has been made in garnets by Fasoli et al., 2011. However, Cd^{2+} ions bring to STE suppressing in alkali-earth fluorides (Radzhabov and Kirm, 2005; Radzhabov et al., 2005). Consequently, Cd^{2+} co-doping leads to suppression of efficient resonance exciton energy transfer mechanism and following light output reducing. Therefore, Cd^{2+} co-doping is not eligible way for increasing light output of $\text{SrF}_2\text{-Ce}$ scintillator. A role of Ga^{3+} and In^{3+} impurities in STE suppressing has not yet been investigated and follow-up study of the crystals doped with Ga^{3+} and In^{3+} ions is required.

4. Conclusion

The SrF_2 crystal are well suited for use as gamma radiation detector. It has a higher (4.18 g/cm^3) than NaI-Tl (3.67 g/cm^3) density, comparable light output, and it is no hygroscopic. Taking into account that crystals $\text{SrF}_2 - 0.3 \text{ mol.}\% \text{ Ce}^{3+}$ and $\text{SrF}_2 - 1 \text{ mol.}\% \text{ Ce}^{3+}$ have a high temperature stability of light output in the temperature interval from -50°C to 200°C , these materials can be applied in well-logging scintillation detectors. Summarizing the experimental results we conclude that strontium fluoride crystals would be useful as newly perspective scintillator.

Acknowledgement

This work was partially supported by Federal Target Program "Scientific and scientific-pedagogical personnel of innovative Russia" in 2009-2013 and Russian Foundation for Basic Research (RFBR).

Authors are thankful to V. Kozlovskii for growing the crystals investigated in this work.

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